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COMPLETE SPECIFICATION

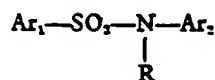
Process for the Production of New Aryl Sulphonic Acid Arylamides

We, J. R. GEIGY A.-G. a body corporate organised according to the laws of Switzerland, of 215, Schwarzwaldallee, Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns new aryl sulphonic acid arylamides having valuable insecticidal properties, processes for the production thereof as well as their use for the protection of keratine material from decomposition by injurious pests. It also concerns, as industrial product, the keratine material protected from decomposition by injurious insects by the use of these compounds.

Various suggestions have already been made for the use of substances which contain sulphon amide groups as insecticides, in particular for the protection of wool and other keratine material from attack by injurious pests. Known compounds of this type however, have the great disadvantage that they develop a sufficient action only against individual types of textile pests, chiefly against the larvae of the clothes moth (*Tineola biselliella*) whilst other equally important textile pests, in particular the larvae of fur and carpet beetles (*Attagenus piceus* and *Anthrenus vorax*) are much less sensitive to these compounds. Thus from the first, no attempt could be made to protect textiles from attack by these organisms, or uneconomically large amounts of the compounds which are active chiefly against the clothes moth must be used in order to attain a certain protective action against the types of beetles mentioned also.

It has now surprisingly been found that aryl sulphonic acid arylamides of the general formula:



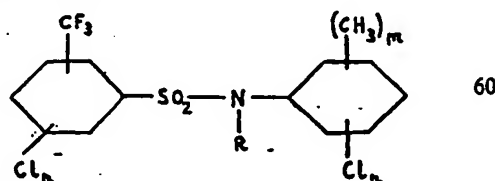
wherein

[Price 3s. 6d.]

Ar₁ and Ar₂ each represent a phenyl radical substituted by at least one trifluoromethyl radical and at least one halogen atom in any one of these phenyl radicals, which radicals, if desired, can be substituted by further halogen atoms, nitro groups and/or by alkyl radicals or alkoxy radicals, and

R represents hydrogen or an alkyl radical, have an excellent insecticidal action not only against the clothes moth and the various stages of development thereof but also against the larvae of the types of beetles mentioned above.

Preferred compounds of the present invention are aryl sulphonic acid arylamides of general formula:



wherein n is 1 or 2, m is 1 or 2 and R represents hydrogen or an alkyl radical.

The compounds defined above can be produced in a simple manner by reacting an aryl sulphonic acid, or aryl sulphenic acid halide of the general formula:



or



with an arylamine of the general formula:



wherein Hal represents chlorine or bromine and Ar₁, Ar₂ and R have the meanings given above. The reaction components are so chosen that at least one of the radicals Ar₁ and Ar₂ contains at least one trifluoromethyl group as

substituent and at least one halogen atom. On the other hand, the radicals Ar_1 and Ar_2 together need not contain any halogen atoms, whence it is necessary for the reaction product to be treated with chlorine or bromine. Again, although the radicals Ar_1 and Ar_2 together contain at least one halogen atom, it may be desired to increase the halogen substitution of the phenyl groups whence the reaction product is treated with chlorine or bromine. The reaction of the aryl sulphonic acid or aryl sulphonic acid halide with the arylamine is performed, if necessary, in the presence of an acid binding agent. If desired, the reaction products obtained in which R is hydrogen, are then treated in the presence of an acid binding agent or after conversion into an alkali metal salt, with a reactive ester of an alcohol. Finally any aryl sulphonic acid arylamides are oxidised by treatment with potassium permanganate.

The reaction of the aryl sulphonic acid or aryl sulphonic acid halides with the arylamines need not be performed in the presence of acid binding agents; both reaction components are reacted advantageously at a raised temperature, possibly in an inert organic solvent as reaction medium. At lower temperatures the reaction can be performed in the presence of an acid binding agent. In a non-aqueous medium examples of such are an excess of the arylamine to be condensed or tertiary organic bases such as for example, pyridine, dimethyl aniline or triethylamine. If desired, these can also serve as solvents; the condensation can also be performed however, in an inert organic solvent such as, for example, benzene, chlorobenzene, toluene, chloroform or diethyl ether.

The reaction can also be performed in an aqueous medium, inorganic bases of the most various type such as, for example, alkali metal-alkaline earth hydroxides, alkali metal carbonates and hydrogen carbonates, phosphates or acetates or organic bases being used as acid binding agents. It is also possible to use solid ion exchangers to bind the hydrohalogenic acid liberated during the reaction.

Examples of aryl sulphonic acid halides suitable as starting products are the chlorides and bromides of 4-chlorobenzene sulphonic acid, 3,4-dichlorobenzene sulphonic acid, 2,3,4-trichlorobenzene sulphonic acid, 2,4,5-trichlorobenzene sulphonic acid, 4-bromobenzene sulphonic acid, 3-trifluoromethyl-benzene sulphonic acid, 3-trifluoromethyl-4-chlorobenzene sulphonic acid, 2,4-dichloro-5-trifluoromethyl benzene sulphonic acid, 2,5-dichloro-4-trifluoromethyl-benzene sulphonic acid, p-toluene sulphonic acid, 3-nitrobenzene sulphonic acid and of 3-nitro-4-chlorobenzene sulphonic acid.

However, also chlorides of aryl sulphonic acids can be used such as, e.g. 4-chlorobenzene sulphenyl chloride, 3,4-dichlorobenzene sulphenyl chloride, 2,4,5-trichlorobenzene sulphenyl chloride, 2-nitro-4-chlorobenzene sulphenyl chloride and 2-nitro-4,5-dichlorobenzene sulphenyl chloride.

Such acid halides can be reacted for example with 4-chloraniline, 3,4-dichloraniline, 3-trifluoromethyl-4-chloraniline, 2,3,4-trichloraniline, 2,4-dichloro-3-trifluoromethyl aniline, 2,5-dichloro-4-trifluoromethyl aniline, 2,3,4,5-tetrachloraniline, 2-trifluoromethyl-4-chloraniline, 2-nitro-4-trifluoromethyl aniline, 2,4,5-trichloraniline, 3,4-dichloro-o-toluidine, 2,4-dichloro-5-trifluoromethyl aniline, 2-amino-4,5-dichloranisole, 2-amino-4-chloranisole, 2-amino-4-trifluoromethyl anisole and 3,5-bis-(trifluoromethyl)-aniline, as well as with the N-methyl and N-ethyl derivatives of these primary amines.

Instead of reacting previously formed aryl sulphenyl halides with the amines defined, also the corresponding mercaptans can be treated with solutions of alkali hypochlorites in the presence of the amine to be acylated so that, after sulphenyl halides are formed as intermediate products, the desired aryl sulphonic acid arylamides are obtained.

The alkyl radical R can be subsequently introduced into aryl sulphonic acid arylamides having a monosubstituted amide group by reacting such aryl sulphonic acid arylamides in aqueous alkaline solution with dimethyl sulphate or diethyl sulphate, or by reacting the alkali metal salts thereof, suspended in organic solvents, with halides such as, for example, butyl bromide.

The aryl sulphonic acid arylamides are oxidised by treatment with potassium permanganate suitably in acetone solution at room temperature.

The compounds of the general formula I produced according to the present invention are relatively only slightly toxic to warm blooded animals. They have considerable fastness to washing on keratine fibres and are excellently suitable for the protection of material consisting of keratine fibres in the natural or treated state, for example, of sheep's wool in the natural or treated state as well as other animal hairs, fells or furs, from attack by clothes moths and textile beetles. As they have considerable fastness to washing on wool, it is possible to attain with them not only a temporary impregnation but also a lasting moth proofing action on keratine textiles such as blankets, woollen carpets, woollen underclothes, woollen top clothes and knitted goods. If the compounds contain a hydrogen atom in the amide group, i.e. if R represents a hydrogen atom, then in the form of their alkali metal salts, they generally dissolve well in water. They can be applied direct from these solutions onto keratine material by soaking the material for a shorter or longer time in the alkali metal salt solutions or spraying it with the alkali metal salt solutions or treating the

material in the alkali metal salt solutions at a raised temperature as in dyeing processes. Compounds which contain no hydrogen atom in the amide group can be drawn on to the keratine material to be protected from their aqueous suspensions or emulsions, advantageously at a raised temperature or such suspensions or emulsions can be sprayed onto the keratine material. Because of the greater solubility of the compounds in organic solvents, they are particularly suitable for incorporation into organic solvents. The solutions obtained can either be used simply by impregnating the material to be protected or, with a suitable choice of solvent and concentration of active ingredient, they can also be used for example as dry cleaning agents.

Those compounds of the general formula I which contain in both phenyl groups a trifluoromethyl radical and which contain one to two chlorine atoms in both phenyl groups as substituents are particularly suitable as active ingredients against pests which are injurious to keratine fibres. There may also be two trifluoromethyl groups in the anilide radical.

First the production according to the present invention of the new aryl sulphonic acid arylamides and then their use for the protection of keratine material are described in more detail in the following examples. In all the examples, parts are given as parts by weight and their relationship to parts by volume is as grammes to cubic centimetres. The temperatures are in degrees Centigrade.

EXAMPLE 1.

58.8 Parts of 2,4,5 - trichloraniline are dissolved in 180 parts of pyridine. 93 Parts of 3 - trifluoromethyl - 4 - chlorobenzene sulphonic acid chloride are added dropwise while stirring and cooling well, the temperature not being allowed to rise over 0°. On completion of the dropwise addition of the sulphonic acid chloride, the mixture is warmed to room temperature. After 8 hours, the mixture is warmed to 70—75° and left at this temperature for 8 hours.

On cooling, the reaction mixture is diluted with about 200 parts of water and the reaction is made strongly alkaline with caustic soda lye whereupon the mixture is distilled with steam. 3 - Trifluoromethyl - 4 - chlorobenzene sulphonic acid - 2¹.4¹.5¹ - trichloranilide is precipitated from the distillation residue with diluted hydrochloric acid. After filtering and drying, it is a grey powder which dissolves easily in caustic soda lye without leaving a residue.

The compound is obtained in completely pure form by recrystallisation from carbon tetrachloride. It melts then at 146—148°.

Under the same reaction conditions, on using stoichiometrical amounts of 2 - amino - 4 - trifluoromethyl anisol and 3,4 - dichlorobenzene sulphonic acid chloride, 3,4 - dichlorobenzene sulphone - 2¹ - methoxy - 5¹ - tri-

fluoromethyl anilide (M.P. 100—102°) is obtained; on using stoichiometrical amounts of 2 - amino - 4 - trifluoromethyl anisol and 3 - trifluoromethyl - 4 - chlorobenzene sulphonic acid chloride, 3 - trifluoromethyl - 4 - chlorobenzene sulphone - 2¹ - methoxy - 5¹ - trifluoromethyl anilide (M.P. 95—97°) is obtained; on using stoichiometrical amounts of 2 - amino - 4 - chloranisol and 3 - trifluoromethyl - 4 - chlorobenzene sulphonic acid chloride, 3 - trifluoromethyl - 4 - chlorobenzene sulphone - 2¹ - methoxy - 5¹ - chloranilide (M.P. 148—150°) is obtained; on using stoichiometrical amounts of 2 - amino - 4,5 - dichloranisol and 3 - trifluoromethyl - 4 - chlorobenzene sulphonic acid chloride, 3 - trifluoromethyl - 4 - chlorobenzene sulphone - 2¹ - methoxy - 4¹.5¹ - dichloranilide (M.P. 126—128°) is obtained and on using stoichiometrical amounts of 3,5-bis-(trifluoromethyl) - aniline and 3 - trifluoromethyl - 4 - chlorobenzene sulphonic acid chloride, 3 - trifluoromethyl - 4 - chlorobenzene sulphone - 3¹.5¹ - bis - (trifluoromethyl) - anilide (M.P. 111—113°) is obtained.

EXAMPLE 2.

a) 44 Parts of 3 - trifluoromethyl - 4 - chlorobenzene sulphone - 2¹.4¹.5¹ - trichloranilide obtained according to example 1 are suspended in 250 parts of water and 48 parts of 30% caustic soda lye are added to the suspension. 25 Parts of dimethyl sulphate are added dropwise at 60—65° to the resultant solution and the reaction mixture is stirred for 3 hours at this temperature. On cooling, the precipitated product is filtered off and dried in the usual way. After recrystallising from ligroin, the 3 - trifluoromethyl - 4 - chlorobenzene sulphonic acid - N - methyl - 2¹.4¹.5¹ - trichloranilide melts at 121—123°.

b) The same compound can be obtained as follows: 63 parts of 2,4,5 - trichloro - N - methyl aniline are dissolved in 100 parts of dimethyl aniline and 150 parts of benzene and the solution is cooled to 5°. At this temperature, 93 parts of 3 - trifluoromethyl - 4 - chlorobenzene sulphonic acid chloride are so added dropwise that the temperature does not exceed 10°. After the dropwise addition of the sulphonic acid chloride, the mixture is warmed to 20° and left for about 5 hours at this temperature; it is then warmed to 65—70° and kept for 8 hours at this temperature.

After cooling, the reaction mixture is poured onto ice and diluted hydrochloric acid. The benzene phase is removed, washed several times with water, dried and concentrated. The residue solidifies in crystalline form and proves to be identical in every respect to the product produced according to a).

EXAMPLE 3.

63.7 Parts of 2,4 - dichloro - 5 - trifluoromethyl aniline are dissolved in 200 parts of

acetone and the solution is diluted with 150 parts of water. 93 Parts of 3 - trifluoromethyl-4-chlorobenzene sulphononic acid chloride are added dropwise at 50—55° to this solution.

5 At the same time 60 parts of 15% caustic soda lye are so added dropwise that the reaction mixture constantly remains weakly alkaline. After stirring for an hour at 50°, the reaction of the mixture is made strongly alkaline by the addition of 30 parts of 30% caustic soda lye. It is then distilled with steam. The residue is acidified with hydrochloric acid and the precipitate is filtered off and washed with water. After drying, the 3-trifluoromethyl-4-chlorobenzene sulphononic acid - 2¹.4¹ - dichloro-5 - trifluoromethyl anilide so obtained is a grey powder. It can be recrystallised from carbon tetrachloride and then melts at 142—145°.

20 Analogously to example 2 under a), this compound can also be reacted with the most various alkylating agents, for example with dimethyl sulphate, diethyl sulphate, butyl bromide.

25 The corresponding compound having an n-butyl radical at the nitrogen atom can be produced as follows: 47.2 parts of 3-trifluoromethyl - 4 - chlorobenzene sulphonic acid - 2¹.4¹ - dichloro - 5¹ - trifluoromethyl anilide (produced according to example 3) are dissolved in 300 parts of dioxan and 17 parts of 30% caustic soda lye are added. 16 Parts of n-butyl bromide in 32 parts of dioxan are added dropwise at 90° within 5 hours. The reaction mixture is then stirred for 15 hours at 90°, diluted with water and, on the reaction being made alkaline, treated with steam. The oily residue is then separated from the aqueous phase, and dried in the vacuum. The dried oily residue is then crystallised from petroleum ether. The 3 - trifluoromethyl - 4 - chlorobenzene sulphonic acid - 2¹.4¹ - dichloro - 5¹ - trifluoromethyl - N - n - butyl anilide obtained in the form of a white powder melts at 96—98°.

Also, for example, 3,4 - dichlorobenzene sulphononic acid - 2¹ - trifluoromethyl - 4¹ - chloranilide (M.P. 112—114°), 3 - trifluoromethyl - 4 - chlorobenzene sulphononic acid - 2¹ - trifluoromethyl - 4¹ - chloranilide (M.P. 106—108°), 3,4 - dichlorobenzene sulphononic acid - 2¹.5¹ - dichloro - 4¹ - trifluoromethyl anilide (M.P. 139—141°), 3 - trifluoromethyl - 4 - chlorobenzene sulphononic acid - 2¹.5¹ - dichloro - 4¹ - trifluoromethyl anilide (M.P. 126—128°), 3 - trifluoromethyl - 4 - chlorobenzene sulphononic acid - 2¹ - nitro - 4¹ - trifluoromethyl anilide (M.P. 151—153°), 2,4,5-trichlorobenzene sulphononic acid - 2¹ - chloro-5¹ - trifluoromethyl anilide (M.P. 106—108°), 3 - trifluoromethyl - 4 - chlorobenzene sulphononic acid - 2¹.3¹.4¹ - trichloranilide (M.P. 131—133°), and 3 - trifluoromethyl - 4 - chlorobenzene sulphononic acid - 3¹ - trifluoromethyl - 4¹ - chloranilide (M.P. 143—145°)

are obtained in the manner described in the above examples.

EXAMPLE 4.

The new insecticidal compounds in which R is hydrogen can be used, for example, in the following manner:

0.8 Parts of active ingredient, for example 3 - trifluoromethyl - 4 - chlorobenzene sulphononic acid - 2¹.5¹ - dichloro - 4¹ - trifluoromethyl anilide, are suspended in 200 parts of water and dissolved with the addition of 5 parts by volume of 1 N-caustic soda lye. The solution is diluted with 3000 parts of water and 100 parts of wool are treated in this liquor for 30 minutes at 60°. After rinsing and drying in the usual manner, the wool proves to be excellently fast to attack by larvae of both the clothes moth as well as of the fur and carpet beetle.

The tests were performed according to the method of the Swiss Association for Standardisation (SNV 95901 and 95902).

EXAMPLE 5.

Two possibilities for the use of compounds in which R does not represent hydrogen are further illustrated below.

a) 1.20 parts of active ingredient, for example 3-trifluoromethyl - 4 - chlorobenzene sulphononic acid - N - methyl - 2¹.4¹.5¹ - trichloranilide, are dissolved in 100 parts by volume of alcohol. This solution is poured into a solution of 5 parts of sulphated castor oil in 4000 parts of water while stirring. 100 Parts of wool flannel are treated for an hour at 100° in the suspension obtained. The fabric is then rinsed and dried in the usual way. On testing, the fabric is excellently proofed against moths and beetles.

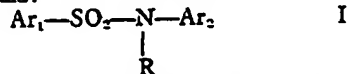
b) The same active ingredient can also be applied while dry cleaning:

10 Parts of active substance are first dissolved in 25 parts by volume of methoxyethanol and this solution is then diluted with 1000 parts by volume of a benzene fraction (for example "Diluan S") suitable for dry cleaning.

The textiles to be treated are dipped in this solution, then squeezed out to 100% content of solvent and dried. After this treatment they prove to be resistant to attack both by moth larvae as well as by fur and carpet beetle larvae.

WHAT WE CLAIM IS:—

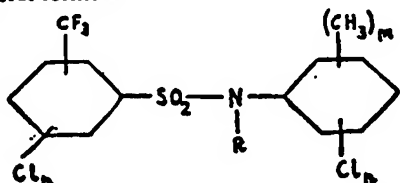
1. Aryl sulphononic acid arylamides of the general formula:



wherein Ar₁ and Ar₂ each represents a phenyl radical substituted by at least one trifluoromethyl radical and at least one halogen atom in any one of these phenyl radicals, which radicals if desired can be substituted by further halogen atoms, nitro groups and/or alkyl radicals or alkoxy radicals, and R represents

hydrogen or an alkyl radical.

2. Aryl sulphonic acid arylamides of the general formula:



5 wherein n represents a whole number from 1 to 2, m represents a whole number from 1 to 2, and R represents hydrogen or an alkyl radical.

10 3. The compound 3 - trifluoromethyl - 4 - chlorobenzene sulphonic acid - 2',4' - dichloro-5' - trifluoromethyl anilide.

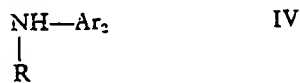
15 4. A process for the production of aryl sulphonic acid arylamides of the general formula I given in claim 1 which comprises reacting an aryl sulphonic acid or aryl sulphonic acid halide of the general formula:



or



20 with an arylamine of the general formula:

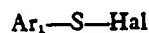


25 wherein Hal represents chlorine or bromine, R represents hydrogen or an alkyl group, the reaction components being so chosen that at least one of the radicals Ar₁ and Ar₂ contains a trifluoromethyl group and at least one halogen atom as substituents and any aryl sulphonic acid arylamides are treated with potassium permanganate.

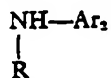
30 5. A process for the production of aryl sulphonic acid aryl amides of general formula I given in claim 1 which comprises reacting an aryl sulphonic acid or aryl sulphonic acid halide of general formula



or



with an aryl amine of general formula



40 wherein Hal and R have the same meanings as in claim 4, the reaction components being so chosen that at least one of the radicals Ar₁ and Ar₂ contains a trifluoromethyl group as substituent, treating the reaction product with chlorine or bromine to substitute the Ar₁ and/or Ar₂ groups and treating any aryl sulphonic

acid aryl amides with potassium permanganate.

6. A process as claimed in claim 4 or 5 in which the reaction is carried out at an elevated temperature. 50

7. A process as claimed in any of claims 4 to 6 in which the reaction is carried out in the presence of an acid binding agent.

8. A process as claimed in claim 7 in which the reaction is carried out in a non-aqueous medium and the acid binding agent is an excess of the aryl amine to be converted or a tertiary organic base. 55

9. A process as claimed in claim 8 in which the acid binding agent also serves as a solvent for the reactants. 60

10. A process as claimed in claim 9 in which the medium is an inert organic solvent.

11. A process as claimed in claim 10 in which the inert organic solvent is pyridine. 65

12. A process as claimed in claim 7 in which the medium is aqueous and the acid binding agent is an organic base.

13. A process as claimed in claim 12 in which the inorganic base is caustic soda. 70

14. A process as claimed in any of claims 4 to 6 in which there is present a solid ion exchanger which binds the hydrohalogenic acid liberated during the reaction.

15. A process as claimed in claim 4 or 5 in which the aryl sulphonic acid is produced *in situ* by treating a mercaptan corresponding to the aryl sulphonic acid with a solution of an alkali hypochlorite in the presence of the amine as defined in claim 4. 75

16. A process as claimed in any of claims 4 to 15 in which the reaction product in which R is hydrogen is treated either in the presence of an acid binding reagent or after converting it to an alkali metal salt, with a reactive ester of an alcohol. 80

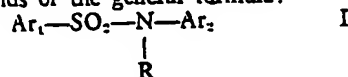
17. A process as claimed in claim 16 in which the reaction product in which R is hydrogen is treated with an aqueous alkali metal solution of dimethyl or diethyl sulphate. 85

18. A process as claimed in any of claims 4 to 15 in which the reaction product in which R is hydrogen is converted to an alkali metal salt and the salt so formed suspended in an organic solvent and reacted with an organic halide. 90

19. A process as claimed in claim 18 in which the organic halide is butyl bromide.

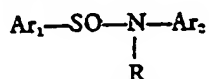
20. A process as claimed in any of claims 4 to 19 in which the halogen substitution of the Ar₁ and Ar₂ radicals in the reaction product is increased by treating the reaction product with chlorine or bromine. 100

21. A process for the protection of keratine material from injurious insects which comprises the application of compositions comprising compounds of the general formula: 105



wherein Ar_1 , Ar_2 and R have the meanings given in claim 1.

22. The keratine material protected from injurious insects by the application of compositions comprising compounds of the general formula:



wherein Ar_1 , Ar_2 and R have the meanings given in claim 1.

23. A process for the production of aryl sulphonic acid arylamides substantially as hereinbefore described in any one of the Examples.

24. Aryl sulphonie acid arylamides substantially as hereinbefore described in any one of the Examples.

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